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Partitioning of hazardous trace elements during coal preparation

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Abstract

The samples of feed coal, cleaned coal, middlings, slime and gangue were collected from Xiqu, Antaibao and Heidaigou coal preparation plants, China. The analyses of minerals, ash, sulfur and 20 hazardous trace elements were performed on the samples by SEM/EDX, INAA, ICP-AES, CV-AAS, GAAS and also on the samples from experimental products (by heavy-media, electrostatic separation and forth-floatation). Partitioning of sulfur and these trace elements under the conditions of different coal ranks and coal preparation types were discussed. The results show that the partitioning behavior of a given element during the cleaning processes is mainly controlled by its modes of occurrence, the distribution forms of its carrier minerals and the cleaning technique types. Although hazardous trace elements have diverse degrees of removal due to different coal ranks and coal preparation types, the elements associated with fine minerals (e.g. Pb, U and Be) and organic constituents (e.g. Br and Cl) will not be effectively reduced by physical coal cleaning and may still be enriched in the cleaned coal. As to the coarse sized feeds (particle size >0.5 mm), the elements associated with coarse/epigenetic minerals can be removed more easily by gravity separation methods and report to the gangue and slime. As to the finer-grained feeds (<0.5 mm), the elements associated with minerals with a high dielectric coefficient are easily removed by electrostatic separation; in comparison with the larger-sized fractions (74–150 μm), the smaller-sized fractions (<74 μm) show a high removability of elements by forth-floatation as a whole. The physical coal cleaning is not only effective in the removal of ash and sulfur, but also in reducing the concentration of most hazardous trace elements. However, as byproducts, the middlings, especially the slimes are preferentially enriched in many hazardous elements (e.g. Cr, Ni and Mo), so that these fractions have a potential of environmental risk and should not be directly used as fuel.

Keywords: coal preparation; hazardous trace elements; partitioning

1. Introduction

The inorganic constituents in coal, comprising dominantly minerals and to a lesser extent amorphous phases and fluid inclusions, are responsible for a series of technological and environmental problems related to coal mining, coal processing such as preparation, combustion, pyrolysis, gasification and liquefaction, and utilization of coal wastes [1]. Coal cleaning, when applied to remove hazardous elements before utilization, is considered an economical and effective technique in minimizing environmental problems [2]. However, only limited information concerning trace element removal is available [3]. Some researchers [4–8] investigated the degree of reduction of

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the twelve inorganic elements as potentially hazardous air pollutants (HAPs) listed in the 1990 US Clean Air Act Amendments by cleaning, and thought that conventional cleaning processes could achieve HAPs rejections of 50–80% [4]. Specific studies have been conducted for As, Hg and Se [9–11].The authors previously studied the partitioning of trace elements in Antaibao coal and Taixi coal, China by size and gravity separation [12–14].

However, further works on the partitioning of trace elements under the conditions of different coal ranks and coal preparation types should be conducted. So, the Antaibao (heavy-media), Heidaigou (jigging) and Xiqu (forth-flotation) coal preparation plants with different separation methods were chosen in this study, of which, the Antaibao and Heidaigou plants are two of the largest steam coal preparation plants with an annual output of nearly 16 Mt, and the Xiqu plant is an important coking coal preparation plant in China. The feeds to the three plants are long flame, gas and coke coals respectively. On the basis of the analyses of ash, sulfur and 30 other major and trace elements (mainly 20 hazardous trace elements) performed on the samples from the plants and also on the samples from the coal preparation experiments (heavy-media, forth-floatation and electrostatic separation), the authors endeavor to discuss the partitioning of these elements during the coal cleaning.

2. Experiments and analytical methods

The representative samples of feed coal, cleaned coal, middlings, slime and gangue were collected from the three plants. Additional samples were derived from the coal preparation experiments.

For the preparation experiments, the feed samples were sieved to obtain >0.5 mm (for heavy-media) and <0.5 mm (for forth-floatation and electrostatic separation) particle size fractions. The <0.5 mm fractions were then ground to 74–150 μm (100-200 mesh) and <74 μm (-200 mesh) to determine their forth-flotation and electrostatic separation cleanabilities at these fine particle sizes. Detailed procedures of heavy-media, electrostatic separation and forth-floatation experiments were described by Wang [12].

Conventional chemical analyses (ash, total and total sulfur and sulfur forms) and the concentration analyses of 30 major and trace elements in the samples were carried out, and As, Br, Cl, Sb, Se, Th and U were determined by instrumental neutron activation analysis (INAA), Al, Ba, Be, Ca, Cr, Cu, Fe, K, Mg, Mn, Mo, Na, Nb, Ni, P, Pb, Sc, Sr, Ti, V and Zn by inductively coupled plasma atomic emission spectroscopy (ICP-AES), Hg by cold-vapor atomic absorption spectrometry (CV-AAS), and Cd by graphite furnace atomic absorption spectrometry (GAAS). Analytical errors were estimated at <5% for most of the elements. Mineralogical analyses of some samples were performed by SEM/EDX.

3. Results and discussion

3.1. Plant samples

Conventional cleaning reduces the contents of many trace elements in varying degrees depending on their modes of occurrences in coal and types of cleaning techniques used. The beneficiation process operates by separating grade on the basis of size, density, and surface chemistry. Heavy-media and jigging separation methods are primarily based on the differences in the density of the material particles, generally requesting the feed sizes >0.5 mm, and forth-flotation relies on the surface properties of coal in separating particles, generally conducted on <0.5 mm particles. Although the elements have different removal efficiencies because of the differences in preparation methods, coal ranks and types, the majority of the hazardous trace elements have a lower content in the cleaned coals than in the feed coals from the plants (Fig. 1). As a whole, the contents of U, Se, Br, Be and Cl are not reduced in the cleaned coals in comparison with the feed coals, even slightly increase, which is obviously associated with their modes of occurrence in coal. According to the previous studies on the analysis of the organic solvent extraction and sequential chemical extraction [12], the authors found that the elements P, U, Se, Br, Be and Cl in the Antaibao coal are likely to be partly associated with organic matter and also with disseminated fine minerals. For instance, the element P mainly occurs in apatite closely enwrapped in coal (Fig. 2b), and fine Cl-bearing minerals are disseminated in the organic portion of coal (Fig. 2c). As for the Heidaigou coal, the element U occur mainly in Zircon in the form of fine grain, and Se and Pb mainly in Galena (PbS), clausthalite (PbSe), and selenio-galena (PbSeS) , as fine-grained fillings in cell cavities (Fig. 2a) [15]. Therefore, these elements are more difficult to be removed by physical preparation and still reserve in the cleaned coals.

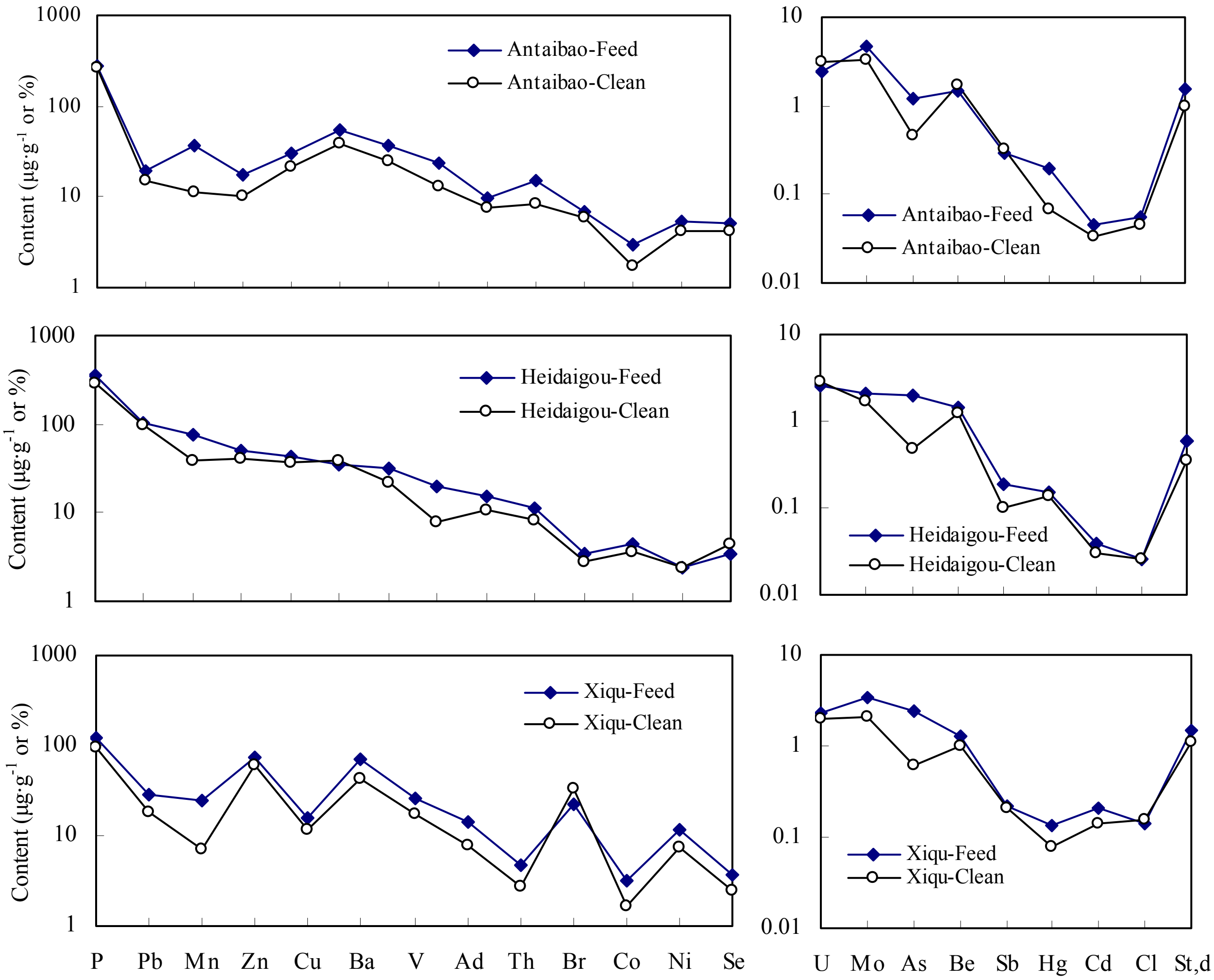

Fig. 1. Contents of ash, sulfur and trace elements in the feed and cleaned coals from the three preparation plants

The partitioning of major and trace elements depends on the degree of liberation of the minerals, their inorganic versus organic association, and the specific gravity of the separation. During the coal cleaning process, coarse-grained minerals are separated from the parent coal to report to the gangue; physically separable fine fractions and mineral fragments falling from the fractures report to the slimes, and the relatively larger density fractions containing many fine-grained minerals closely associated with the organic constituents report to the middlings. Hence, most elements have higher contents in the slime (especially Ba, Cr, Ni and Mo), gangue and middlings than in the feed coal (Fig. 3), suggesting their association with minerals. In China, the middlings are generally used as part of the feed to coal-fired power plants and the coal slime is usually as feed to heat and power plants and civil fuel. However, it is clear that the potential environmental risks of the middlings and slime are higher than those of the raw coal in direct utilization. Some elements such as Sr, Pb, Mn, Zn, Fe, Ca and Mg, which possibly occur as dissolved salts or inorganic elements incorporated within the organic compounds, are relatively enriched in the Heidaigou feed coal in comparison with the byproducts (Fig. 3).

3.2. Heavy-media and electrostatic separation experiment analyses

Fig. 4 shows that the elements distribute in the cleaned coals from the heavy-media and electrostatic separation experiments for the Antaibao coal. It is found that the majority of the hazardous trace elements have diverse degrees of removal during the cleaning processes. The elements Pb, Ba, V, Cr, Co, As, Hg, Cd, Fe, S have a relatively high degree of removal during heavy-media experiments, indicating their strong affinities with coarse minerals. However, the contents of P, Mn, Zn, Cu, Br, U, Mo, Be and Cl in the heavy-media cleaned coal did not decrease in comparison with the feed coal, even increase, especially for Zn and Cu, possibly resulting from some experimental errors or from the adsorption of Zn and Cu ions in process water by the coal [14]; the distributions of the other elements such as P, U, Se, Br, Be and Cl are basically similar to their distributions in the cleaned coals from the Antaibao preparation plant (Fig. 1).

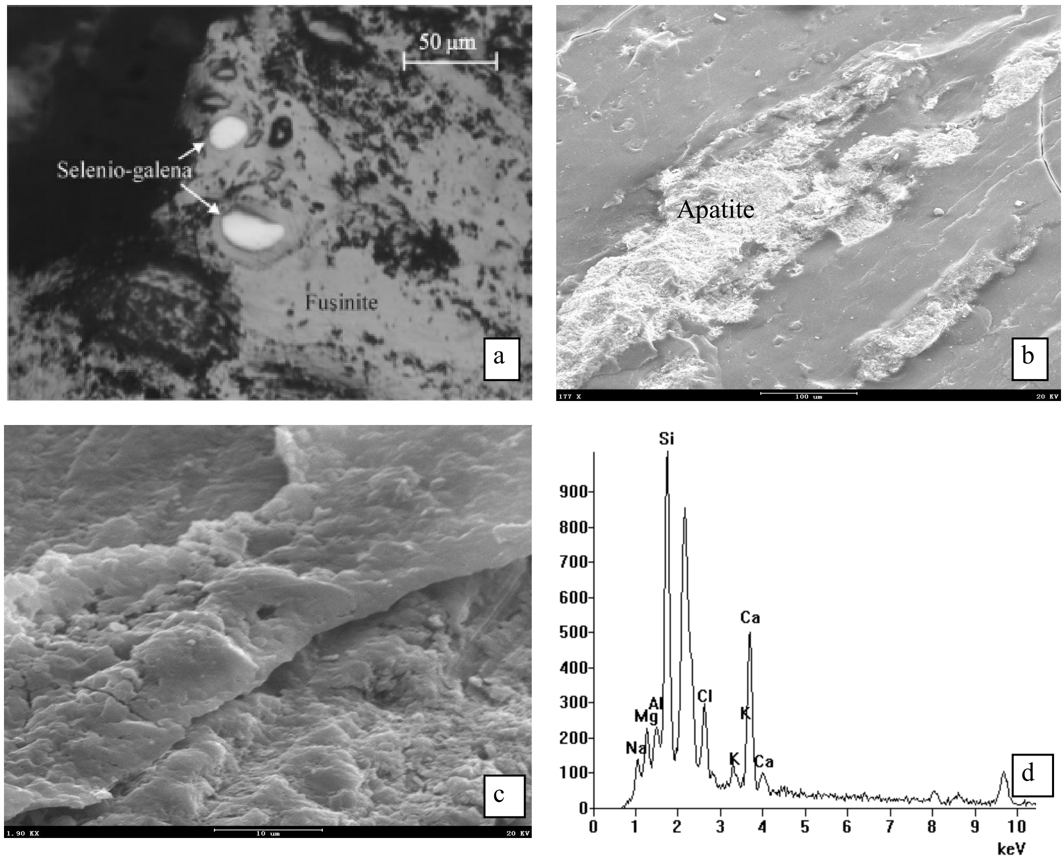

Fig. 2. Morphology of minerals in coal. (a), selenio-galena particles filled in fusinite cell cavities, reflected light, after Dai et al.[15]; (b), apatite closely enwrapped in the organic constituents, SEM; (c), fine Cl-bearing minerals disseminated in the organic constituents, SEM; (d), EDX analysis of (c)

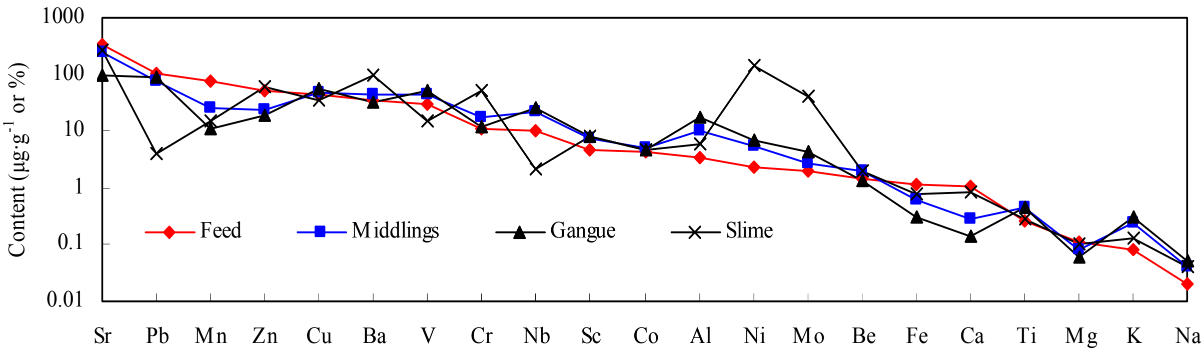

Fig. 3. Contents of elements in the feed coal, middlings, gangue and slime from Heidaigou preparation plant

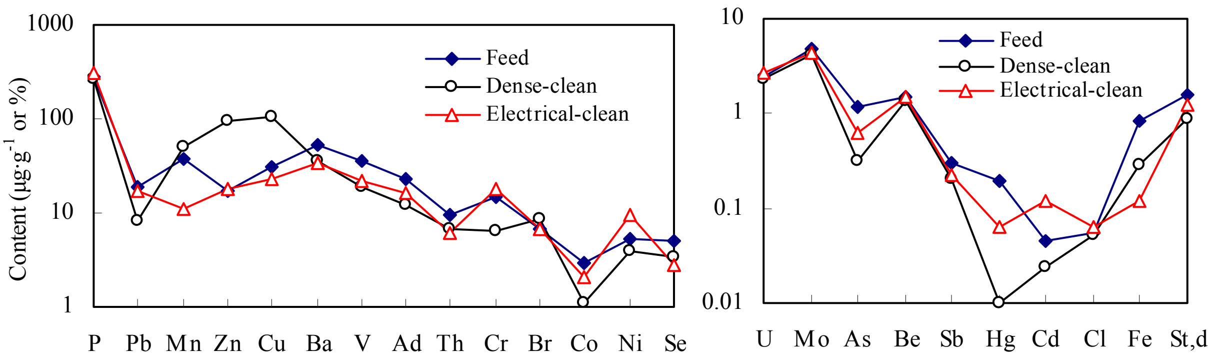

Fig. 4. Contents of hazardous trace elements in the cleaned and feed coals from the heavy-media and electrostatic separation experiments for the Antaibao coal

Electrostatic separation is a dry beneficiation technique involving imparting a charge onto fine particles and separating the particles toward electrodes, dominantly relying on the electrical property difference of fine particles. As shown in Fig. 4, the contents of P, Mn, Zn, Cu, Br, U, Mo, Be and Cl do not obviously decrease in the electrostatic separation cleaned coal in comparison with the feed, while the others show a higher degree of removal, especially Fe, Mn and Th, even their electrostatic separation cleanability greater than heavy-media cleanability, possibly mainly associated with pyrite and clay minerals. Among common minerals of coal, pyrite and clay minerals possess a relatively higher dielectric constant (Table 1), hence showing a good removal efficiency.

Table 1. Dielectric constants of common minerals in coal

Minerals	Pyrite	Kaolinite-Clay minerals	Calcite	Gypsum	Quartz
Dielectric constants	46.92	34.27–36.66	7.54	5.17	4.65

3.3. Flotation experiment analysis

For the same kind of coal, flotation separation efficiency is different for different size fractions. Fig. 5 exhibits forth-flotation cleanabilities at two fine particle size fractions (74–150 μm and <74 μm) of the Antaibao coal. It is obviously observed that the elements Mn, Co, Ni, Th, Cr, Be and Cd are not removed efficiently at the 74–150 μm size, but can be partly removed at the <74 μm size. This suggests these elements are associated with finer-grained minerals, and their reduction effectiveness depends in part on the particle size of the host minerals and the extent to which they are liberated from the organic matter when the coal is crushed.

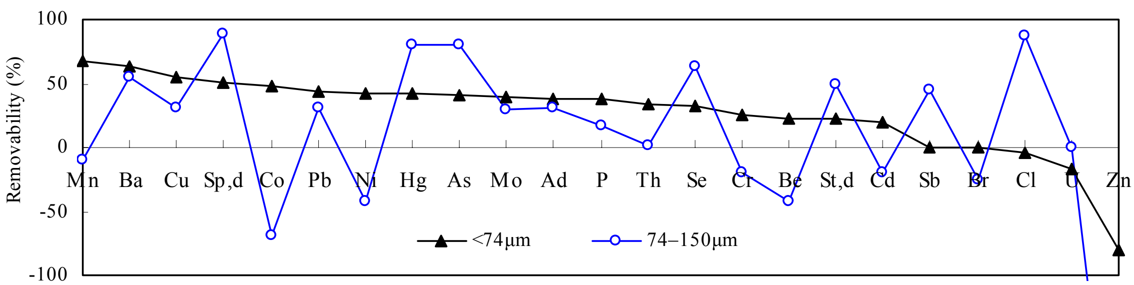

Fig. 5. Removabilities of ash, sulfur and hazardous trace elements in 74–150 μm and <74 μm sizes (removability= 1-an elemental content in cleaned coal/ the elemental content in feed coal)

4. Conclusions

1) The partitioning behavior of a given element during the cleaning processes is mainly controlled by its modes of occurrence, the distribution forms of its carrier minerals and the cleaning technique types. Although hazardous trace elements have diverse removabilities due to different coal ranks and coal preparation types, the elements associated with fine minerals (e.g. Pb, U and Be) and organic constituents (e.g. Br and Cl) will not be effectively reduced by physical coal cleaning and may still be enriched in the cleaned coal.

2) As to the coarse sized feeds (> 0.5mm), the elements associated with coarse/epigenetic minerals can be removed more easily by gravity separation methods and report to the gangue and slime. As to the finer-grained feeds (particle size <0.5 mm), the elements associated with minerals with a high dielectric coefficient are easily removed by electrostatic separation; in comparison with the larger-sized fractions (74–150 μm), the smaller-sized fractions (<74 μm) show a high removability of elements by forth-floatation as a whole.

3) The physical coal cleaning is not only effective in the removal of ash and sulfur, but also in reducing the concentration of most hazardous trace elements. However, as byproducts, the middlings, especially the slimes are preferentially enriched in many hazardous elements (e.g. Cr, Ni and Mo), so that these fractions have a potential of environmental risk and should not be directly used as fuel.

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